Supplementary Information

Nanoparticle shapes of $LiMnPO_4$, Li^+ diffusion orientation and diffusion coefficients for high volumetric energy Li^+ ion cathodes

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Electrochemical potential spectroscopy (EPS) Experimental method

The lithium ion diffusion coefficient was measured in a three-electrode open cell with lithium counter and reference electrodes with 1M $LiPF_6$ in EC/DMC (Sigma) inside a grounded Faraday cage housed in an argon glovebox. Electrochemical control and measurement were performed using a Bio-Logic SP-300 potentiostat.

Electrochemical Potential Spectroscopy (EPS) is a variant of Potentiostatic Intermittent Titration Technique (PITT) where there is no open-circuit period applied between voltage steps. EPS was performed through chronoamperometric response measurements as 5 mV step voltages are applied. Charging measurements (lithium extraction) start from the initial open-circuit potential, the applied voltage is step-wise increased every 3 minutes until 4.4 V (vs. Li/Li^+). For the discharge portion (lithium insertion), it is decreased instead, also in 5 mV steps, held for 3 minutes each until 2.5 V (vs. Li/Li^+).

The current transient response to applied step potential is described by the equation below, where *l* as the electrode thickness, *F* is Faraday's constant and *S* is the electrode surface area. To avoid the need to calculate the difference between the concentration of the lithium ions at the surface (C_s) and bulk (C_o), the EPS-derived lithium ion diffusion coefficient ($\widetilde{D}_{\mathrm{Li,EPS}}$) was calculated from the slope of the linear portion of the natural log of the current transient ln(*i(t)*) vs. time *t*. As the slope equates to $\left(-\frac{\pi^2 \widetilde{D}_{\mathrm{Li,EPS}}}{4l^2}\right)$, the $\widetilde{D}_{\mathrm{Li,EPS}}$ can be calculated.

$$i(t) = \frac{2FS(C_s - C_o)\widetilde{D}_{\mathrm{Li,EPS}}}{l} \exp\left(-\frac{\pi^2 \widetilde{D}_{\mathrm{Li,EPS}}}{4l^2} t\right)$$

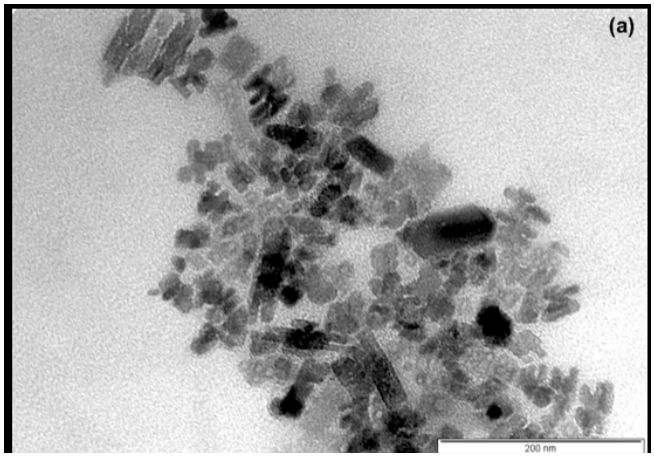

Fig. S1. TEM image of $LiMnPO_4$ particles synthesized with manganese acetate.

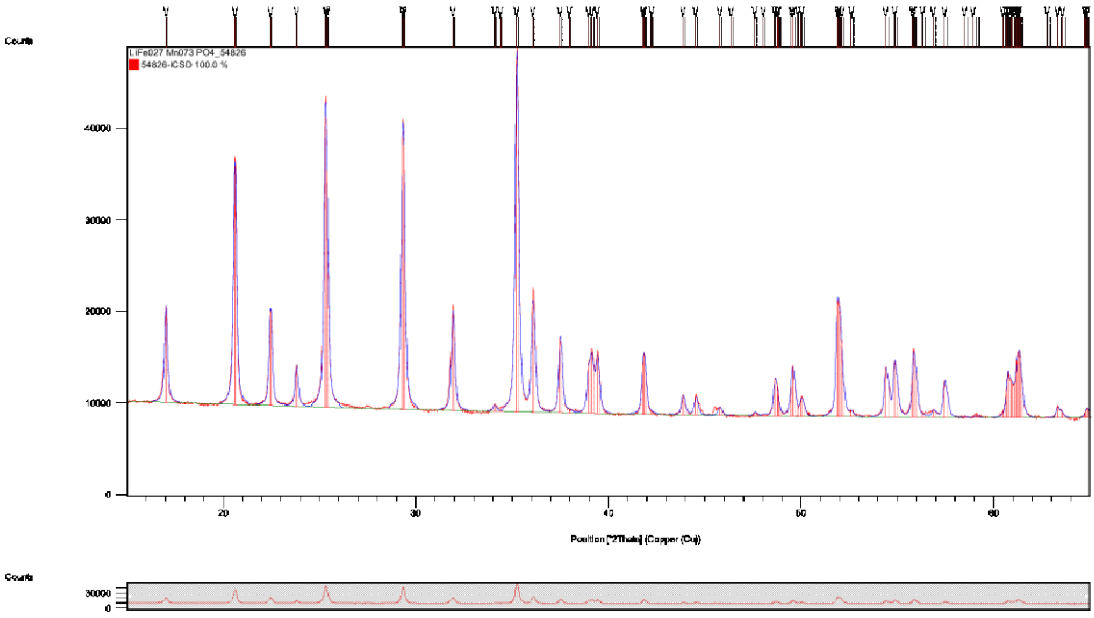

Fig. S2. Rietveld refinement analysis of nano-$LiMnPO_4$. The red is experimental and the blue is calculated. The reliablility factors, Rwp (weighted profile R-factor) = 1.9663, Rexp (expected R-factor)= 0.9665, Rp= 1.4447, GOF (goodness of fit) = 4.1388.

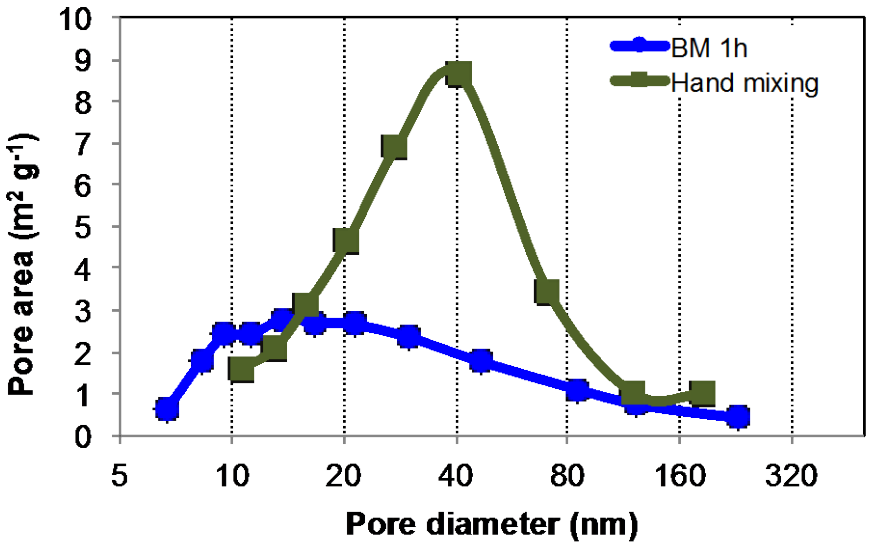

Fig. S3. The pore size distribution of the composites, nano-$LiMnPO_4$ and carbon prepared by hand mixing and ball milling.